DA: 1B262301A300
AMCMS Code: 522A.11.62400
HDL Proj: CMT 91

HDL-TR-1552

EPOXY CURING AGENTS

II. DEACTIVATED IMIDAZOLES AND FLEXIBLE SYSTEMS

by

Thomas J. Dearlove

July 1971

U.S. ARMY MATERIEL COMMAND
HARRY DIAMOND LABORATORIES
WASHINGTON, D.C. 20438

ABSTRACT

Imidazole-type compounds will cure epoxy adhesives under moderate conditions and impart a relatively high heat resistance to the product. Various means of increasing the pot life to permit extended storage prior to use were studied. These included deactivation of the imidazole ring with chloro, nitro, and cyano groups which rendered the catalyst inactive toward epoxy resins, microencapsulation of imidazoles, also unsuccessful, and use of imidazole salts which yielded a heat-resistant adhesive but required high curing temperatures.

The mechanisms of imidazole curing of two flexible epoxy systems, one a polyesterurethane elastomer system, and the other a polysulfide rubber system, were studied by means of infrared and nuclear magnetic resonance spectroscopy. A novel side reaction involving the imidazole catalyst in the polysulfide rubber system is discussed.

CONTENTS

TABLES

ILLUSTRATIONS

Figure

1. INTRODUCTION

Imidazole-type compounds cure epoxy adhesives under moderate reaction conditions to yield materials having a fairly high heat resistance. The pot life of the imidazole-epoxy resin system under refrigeration is longer than that observed with other room-temperature curing agents. However, when imidazole-catalyzed epoxy resins are cured in bulk, the reaction is highly exothermic thereby limiting their use to small-volume applications such as adhesives.

An earlier report (ref 1) describes the proposed mechanism for an imidazole cure (fig. 1), and compares several commercially available imidazoles with respect to heat deflection temperature, bond strengths, and thermal properties of the cured resin. The present investigation is an extension of the earlier work. A series of deactivated imidazoles was prepared in order to determine if the pot life of the mixed adhesives could be extended while still maintaining an acceptable cure rate. The compounds were deactivated through introduction of electron-withdrawing groups on the ring as well as by the positioning of bulky substituents on the 2-position of the ring. Another type of deactivated imidazole, an imidazole lactate salt, was also prepared and tested.

In another approach to extension of pot life an attempt was made by an industrial concern to encapsulate liquid and solid imidazoles, at the request of these laboratories.

The uses of imidazole compounds in the copolymerization of epoxy resin with a polyesterurethane elastomer and with a polysulfide rubber were also investigated. The former system, a mixture of an epoxy resin, a polyesterurethane elastomer in tetrohydrofuran (THF), and 2-ethyl-4-methyl imidazole, had been under investigation in this laboratory (ref 2) and showed promise as a flexible coating or adhesive.

Commercial literature available on such a flexible epoxy system reported the use of 2.5-10 percent epoxy resin with dicyanamide as the curing agent (ref 3) and the use of a high ratio of epoxy resin to polyurethane (ref 4), again with a dicyanamide curing agent. In the former case, it was stated that some cross-linking occurred through the urethane bridge, whereas in the latter case no mention of cross-linking was made. In this laboratory a 60:40 epoxy—polyurethane system is employed. It was desirable to determine whether cross-linking was occurring in this system when imidazoles were used as curing agents. This was accomplished by following the cure with infrared absorption spectroscopy.

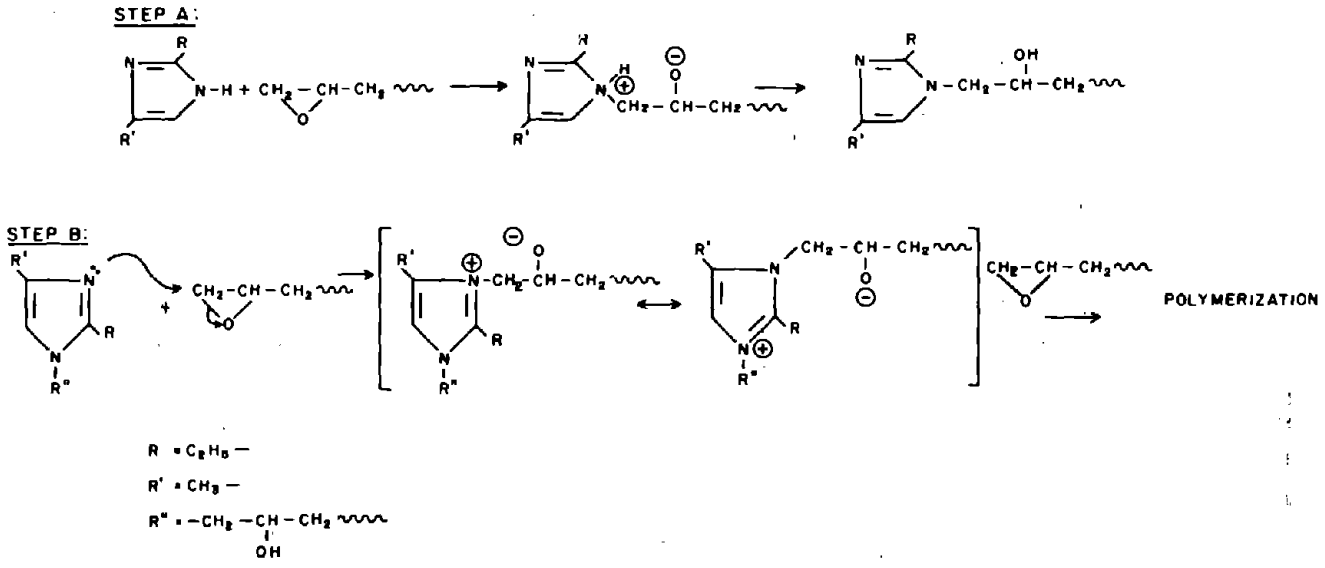
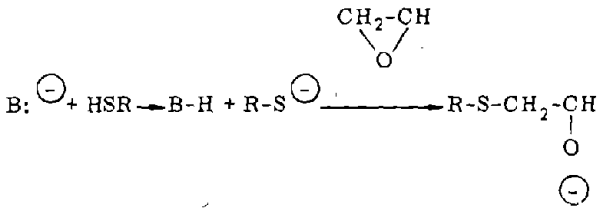


Figure 1. Mechanism for the polymerization of a polyepoxide with 2-ethyl-4-methylimidazole

A polysulfide rubber flexibilizer is essentially a long-chain molecule containing mercaptan groups (-SH) at either end. Polysulfide rubber reacts very slowly with an epoxy resin. However, when a moderate excess of epoxy resin is polymerized with a primary or tertiary amine in the presence of a polysulfide rubber, a flexible epoxy resin is obtained (ref 5). The reactivity of the mercaptan groups is enhanced by the presence of a base such as an amine or the alkoxide ion of an opened epoxide ring. The base abstracts the proton of the mercaptan leaving a mercaptide ion which readily attacks an epoxide ring and thus becomes incorporated in the polymer network.



In view of the proposed mechanism for the imidazole cure of epoxy resins (fig. 1), it was expected that the imidazole compounds would also cure an epoxy-polysulfide system. An investigation unexpectedly showed that some imidazole compounds effected a cure in this system while others did not.

2. EXPERIMENTAL METHODS

2.1 Physical Methods

Melting points were determined using an electrically heated oil bath and are in °C.

The infrared absorption measurements were obtained using a Beckmann IR-5 spectrophotometer. Liquid samples were run neat, and solid samples, in a mineral oil mull.

Nuclear magnetic reasonance spectra were obtained on a Varian A-60 using carbon tetrachloride as a solvent and tetramethyl silane as a reference.

Viscosity measurements were obtained by comparison with Gardner bubble tube viscometers. The gel time at room temperarure for a diluted epoxy resin of the bisphenol-A-epichlorohydrin type (weight per epoxide 175-195) catalyzed with imidazole compounds was determined by following the change in viscosity with respect to time. When the samples reached a point where there was no visible flow in an hour's time, they were considered unworkable and at their gel point.

Analysis by gas chromatography was performed using a Varian Aerograph Model 1520 utilizing a 6 ft by 1/8 in. stainless steel column packed with 20 percent Silicone SE 30 on Chromsorb G with helium as the carrier gas.

Bond strength measurements were obtained according to ASTM D-2095 using a universal testing machine and 1-in. tall cylindrical aluminum plugs of 0.25 sq. in. surface area. The machine was loaded at a crosshead speed of 0.05 in. per min, and the load versus elongation was recorded on a strip chart as described previously (ref 1).

Heat deflection temperature was measured according to ASTM-D-648-56 using a heat deflection temperature tester in which five specimen bars (5 by 1/2 by 3/8 in.) were each subjected to a load of 264 psi, as described previously (ref 1).

2.2 Preparation of Deactivated Imidazoles

Figure 2 shows the generalized scheme for the preparation of the deactivated imidazole compounds. Table I lists physical properties of the deactivated imidazoles that were prepared.

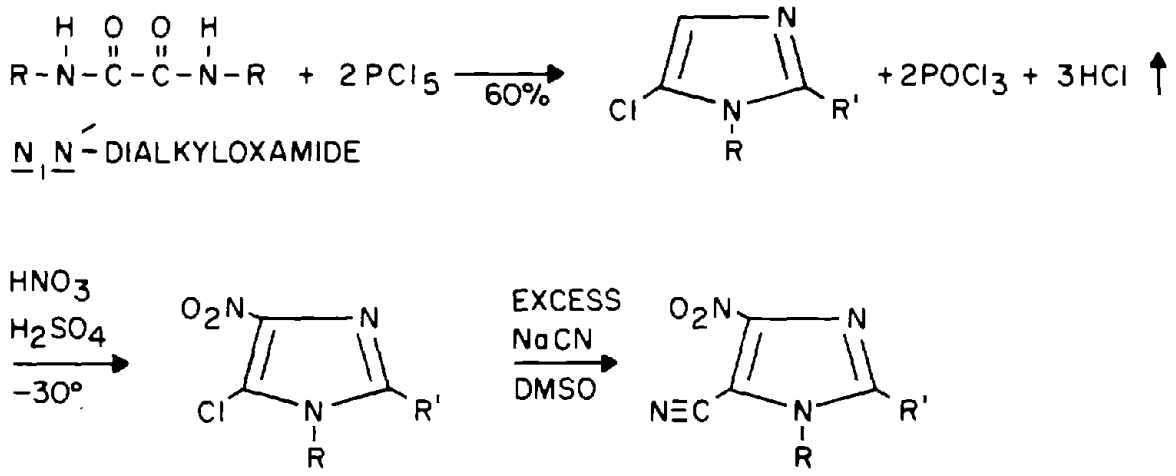


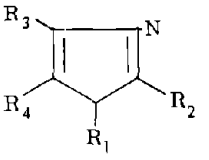
Figure 2. Preparation of deactivated imidazole compounds

2.2.1 Preparation of Starting Material, N,N'-Dialkyloxamides

The following starting materials were obtained from commercial sources and used without further purification: diethyloxalate, methylamine (40 percent aqueous solution), ethylamine, butylamine, and phosphorous pentachloride.

A general procedure for the preparation of the N,N'dialkyloxamides (ref 6,7) was as follows: a solution containing 100 g (2.2 moles) of ethylamine in 100 ml of ethanol was slowly added with stirring to a chilled solution of 146 g (1.0 mole) of ethyloxalate in 1000 ml of ethanol. The solution was

Table I. Deactivated Imidazoles



Compound	R_1	R_2	R_3	R_4	m.p. (Recrystallization solvent) or b.p. (Pressure in mm)	
					FOUND (°C)	LITERATURE (°C)
A	$-CH_3$	-H	-H	-Cl	125-130° (60)	204 -205° (760) ref 8
B	$-C_2H_5$	$-CH_3$	-H	-Cl	58- 60° (0.7)	228 -232° (620) ref 7
C	$-C_4H_9$	$-C_3H_7$	-H	-Cl	158-159° (30)	252 -256° (620) ref 7
D	$-C_2H_5$	$-CH_3$	$-NO_2$	-Cl	88- 90° (CCl_4)	88 -89° (-) ref 7
E	$-C_4H_9$	$-C_3H_7$	$-NO_2$	-Cl	33- 35° (Ethanol-water)	34.5-36.0° (-) ref 7
F	$-C_2H_5$	$-CH_3$	$-NO_2$	-CN	78- 80° (Ethanol)	78 -79° (-) ref 7

A = 5-chloro-1-methylimidazole

B = 5-chloro-1-ethyl-2-methylimidazole

C = 1-butyl-5-chloro-2-propylimidazole

D = 5-chloro-1-ethyl-2-methyl-4-nitroimidazole

E = 1-butyl-5-chloro-4-nitro-2-propylimadazole

F = 5-cyano-1-ethyl-2-methyl-4-nitroimidazole

stirred overnight at room temperature, and the resulting white precipitate was collected by suction filtration. After air drying, the diethyloxamide (m.p. 177-178°C) was found pure enough for the next reaction. A total of 138 g (96 percent) was obtained.

2.2.2 Preparation of Chloroalkylimidazoles

The following is a general procedure for the preparation of 1,2-dialkyl-5-chloroimidazoles. These reactions were carried out in a fume hood with a suitable trapping system since copious amounts of hydrogen chloride gas were evolved during the reaction.

In a 2-liter flask fitted with a water condenser and drying tube was placed 144 g (1.0 mole) of N,N'-diethyloxamide and 416 g (2.0 mole) of powdered phosphorous pentachloride. The reactants were intimately mixed. After several minutes a vigorous reaction took place which continued until no solid material remained. The dark solution was heated on a hot water bath for 5 hr, cooled and transferred to a 1-liter flask. The phosphorous oxychloride that was formed during the reaction was distilled off under reduced pressure (b.p. 35-40°C at 20-25 mm). The black residue remaining in the distillation pot was chilled to -5°C and decomposed by the very cautious addition of 150 ml of cold water. The aqueous solution was then chilled, made strongly alkaline with 50-percent sodium hydroxide solution, and extracted with four 300-ml portions of chloroform. The chloroform extracts were combined and extracted with four 200-ml portions of 4N hydrochloric acid solution. The acid extracts were combined, washed with fresh chloroform, chilled and made strongly alkaline with 50-percent sodium hydroxide solution. The alkaline solution was extracted with four 300-ml portions of chloroform, which were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the dark residue, distilled (b.p. 68-70°C at 0.4 mm). Redistillation gave 110g (77 percent) of 5-chloro-1-ethyl-2-methylimidazole, b.p. 58-60°C (0.7 mm).

2.2.3 Preparation of Chloronitroalkylimidazoles

The following method for the preparation of 5-chloro-1-ethyl-2-methyl-4-nitroimidazole is a general procedure for the nitration of chloroalkylimidazoles.

To a 1-liter round bottom flask containing 51.0g (0.35 mole) of 5-chloro-1-ethyl-2-methylimidazole chilled to -30°C, was very cautiously added 400 ml of a cold 1:3 nitric acid-sulfuric acid mixture. The initial reaction was very exothermic, and a thick white smoke evolved. After approximately 100 ml of acid mixture had been added, the violence of the reaction subsided, and a characteristic brown smoke of a nitrogen oxide gas was observed. After the addition was completed, the mixture was heated in a hot water bath for 4 hr and then allowed to cool to room temperature. The

acid solution was slowly poured into 2.5 liters of ice water, and the resulting clear, pale-green solution was extracted with several portions of chloroform. The combined extracts were dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The residue, a pale-green oil, was crystallized from carbon tetrachloride to give 5-chloro-1-ethyl-2-methyl-4-nitroimidazole as a white granular solid, m.p. 88-90°C. A total of 48 g (74 percent) was obtained.

2.2.4 Preparation of the Cyanonitroalkylimidazole

In a 500-ml round-bottom flask fitted with a drying tube was placed 30.0 g (0.15 mole) of 5-chloro-1-ethyl-2-methyl-4-nitroimidazole, 9.0 g (0.15 mole) of anhydrous sodium cyanide, and 300 ml of anhydrous dimethylsulfoxide. The solution was stirred 24 hr at room temperature and then heated for 2 hr in a hot water bath. The dark brown solution was cooled, poured into 1 liter of water, and continuously extracted with ethyl ether. After 48 hr the ether extract was washed once with cold water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to yield 16.5 g of pale-yellow crystals. Recrystallization from ethanol gave 14.0 g (55 percent) of pure 5-cyano-1-ethyl-2-methyl-4-nitroimidazole.

2.3 Preparation of Imidazole Lactate Salts

The following is a general procedure for the preparation of imidazole-type carboxylate salts.

Over a 15-min period, 53 g (0.5 mole) of 85-percent lactic acid solution was added, with stirring, to 34 g (0.5 mole) of imidazole. The clear, pale-yellow solution that resulted was heated to 70-80°C for an hour to complete the reaction. The material crystallized after several days, but purification was not attempted. The white salt was readily soluble in epoxy resins. For more convenient handling, it could be melted in an oven at 65°C and then would remain in the liquid state for extended periods of time.

The use of excess lactic solution with the salt resulted in less tendency for the salt to crystallize on standing, as well as a longer pot life when the mixture was incorporated in an epoxy resin at room temperature.

2.4 Microencapsulation of Imidazole

Attempts at encapsulating 2-ethyl-4-methylimidazole (EMI-24), 1-methylimidazole (MI-1), and imidazole were made by National Cash Register Co. All attempts to encapsulate the liquid curing agents, EMI-24 and MI-1, were unsuccessful, whereas attempts to encapsulate imidazole (m.p. 90°C) using a copolymer of polyethylene and vinylacetate were successful. Two samples were obtained utilizing 10 and 20 percent by weight of wall material.

Determination of the leakage of the capsules was performed by extracting them with water. Material remaining after evaporation of the water extract was compared with authentic imidazole by infrared spectroscopy and mixed melting point.

2.5 Imidazole Compounds as Catalysts for an Epoxy-Polyurethane System

2.5.1 Formulation

A solution containing 8 g of a polyesterurethane elastomer* and 50 g of tetrahydrofuran was prepared. To the homogeneous solution was added 12 g of a bisphenol-A-epichlorohydrin epoxy resin (weight per epoxide 185-192) and 1.2 g of 1-methylimidazole. This solution remained active for several months when stored under refrigeration.

2.5.2 Analysis by Infrared Spectroscopy

A thin film of the tetrahydrofuran solution was allowed to air-dry on a sodium chloride crystal. Changes in structure were observed by scanning its infrared spectrum at various points in the cure cycle of the sample.

2.6 Imidazole Compounds as Catalysts for an Epoxy-Polysulfide Rubber System

2.6.1 Formulation

In the investigation of this system, an undiluted epoxy resin of the bisphenol-A-epichlorohydrin type (weight per epoxide 185-192) was used in conjunction with a polysulfide rubber having a molecular weight of approximately 1000 g/mole and functionality of approximately 2.

The addition product of 1-methylimidazole and phenyl glycidyl ether was prepared by the slow addition of 30 g (0.2 mole) phenyl glycidyl ether to a dilute solution containing 16 g (0.2 mole) of 1-methylimidazole in 200 ml of benzene. After heating this solution to reflux temperature for 2 hr, the solvent was removed on a rotary evaporator leaving a dark red-brown oily residue. The infrared spectrum of the product showed the loss of absorption at 920 cm^{-1} (oxirane) indicating complete reaction.

Analysis by gas chromatography indicated that the oily residue was essentially one component and contained, at most, only negligible amounts of 1-methylimidazole.

*ESTANE 5701, B. F. Goodrich C.

A mixture containing 25 g of isopropyl glycidyl ether, 5 g of polysulfide rubber and 2 g of 1-methylimidazole was allowed to stand at room temperature for 2 days. The mixture was then heated at 100°C for 4 hr at which time no further change in its IR spectrum was observed. Distillation of the mixture yielded 8.0 g of isopropyl glycidyl ether, b.p. 30°C (2 mm); 0.3 g of a mixture of materials, b.p. 70-73°C (0.2 mm) and 4.7 g of a clear, pale-yellow liquid, b.p. 130-145°C (0.2 mm). No further distillate could be obtained from the pot residue. The IR spectrum of the high boiling fraction showed strong absorptions at 3450 cm^{-1} (-OH) and 1665 cm^{-1} (unknown).

2.6.2 Analysis by Infrared Spectroscopy

Analysis of starting materials and products of the cure were obtained by placing a thin film of sample between two sodium chloride crystals. The loss or appearance of absorption was followed by scanning the spectrum of the sample at various times during the cure.

Standard characteristic regions in this particular system are: 3400-3500 cm^{-1} (hydroxyl group), 2500 cm^{-1} (mercaptan group), 1650-1700 cm^{-1} (See section 3.5), and 920 cm^{-1} (oxirane group).

3. RESULTS AND DISCUSSION

3.1 Preparation and Testing of Deactivated Imidazoles

The general method for the preparation of dialkyloxamides and their subsequent reaction with phosphorous pentachloride to yield chloroalkyl substituted imidazoles has been reported in the literature (ref 8,9). A further investigation into the specific structure of the chloroalkylimidazoles and some reactions that these compounds undergo has been reported recently (ref 6,7).

The series of deactivated imidazoles that was prepared (table I) was chosen for several reasons. First, the compounds were an unique combination of electron withdrawing groups (i.e., chloro, nitro, and cyano) and various bulky alkyl substituents on the 2-position of the ring. Both of these kinds of substituents would exert some degree of deactivation on the active tertiary-type nitrogen in the 3-position of the imidazole ring. This would allow a comparison of the variously deactivated imidazoles with each of the variously deactivated imidazoles, with each other, and with the commercially available imidazole curing agents. Second, the deactivated imidazoles were either liquid or low melting solids (table I) and, hence, could easily be mixed with the epoxy resin. Third, the sequence by which the compounds were prepared is a

relatively simple and convenient route. The yields of product were usually high, and purification was not a problem.

As shown in table I, the boiling points of the liquid imidazoles were determined at pressures lower than those reported in the literature. However, confirmation of their structure was effected through comparison of their infrared spectra with reported spectra, and also by the fact that they gave solid imidazole compounds whose melting points and infrared spectra compared with the literature values.

Figure 3 compares the rate of cure at room temperature of three deactivated imidazole compounds and the three commercially available imidazoles.

The substitution of a chloro group on the ring extended the pot life of the mixed epoxy-imidazole system to twice that observed for 2-ethyl-4-methylimidazole (EMI-24). In the case of 1-butyl-5-chloro-2-propylimidazole, the gel time was over ten times as long. The chloronitro and nitrocyano substituted imidazoles were so deactivated that they yielded virtually no change in viscosity at room temperature. Their lack of activity was proven by failures in all attempts to cure epoxy resins with them at temperatures in excess of 100°C. Further testing of the chloronitro and cyanonitro substituted imidazoles was terminated.

Of the chloroalkylimidazoles prepared, the 5-chloro-1-ethyl-2-methylimidazole showed the greatest reactivity at room temperature; hence, it was chosen as the group-representative in further testing. Table II shows the results of bond strength testing, and table III shows the results of heat deflection temperature measurements. In these tests, 4 parts per 100 of 5-chloro-1-ethyl-2-methylimidazole were mixed with an epoxy resin of a bisphenol-A-epichlorohydrin type.

In curing the test samples for the measurements of bond strength, it was found that a cure cycle of 4 hr at 149°F was not successful in effecting a cure. After 20 hr at 149°F, the samples had very poor bond strength. A postcure for 4 hr at 300°F greatly improved the results.

The heat deflection temperature for a sample cured initially at room temperature, and postcured for 6 hr at 149°F, was extremely low. When a sample was postcured at 300°F, it softened and deformed so that it was not suitable for testing. A new sample was not prepared because the above bond strength tests indicated an excessive cure temperature requirement.

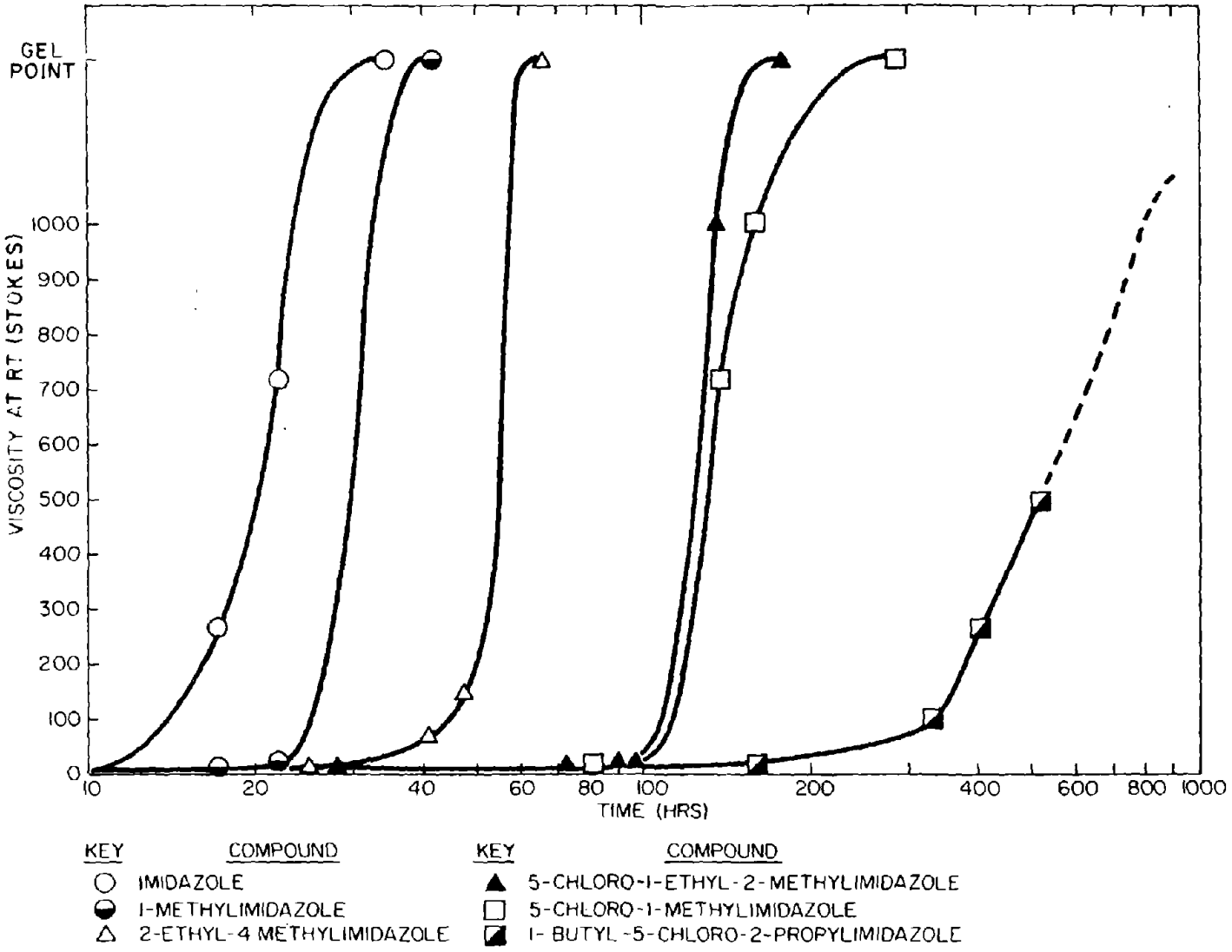


Figure 3. Change in viscosity at room temperature of a series of imidazole compounds

Table II. Bond Strength of Epoxy Adhesives at Room Temperature

Curing Agent*	Cure Cycle (°F)	Bond Strength (psi)
5-Chloro-1-ethyl-2-methylimidazole	20 hr/149°	1345
	20 hr/149° + 4 hr/300°	4220
Imidazole Lactate (1:1)	5 hr/149°	2300
	5 hr/149° (8phr)	3530
	20 hr/149° + 4 hr/300°	6400
Imidazole Lactate (1:1.7)	20 hr/149°	3310
	20 hr/149° + 4 hr/300°	8000**
1-Methylimidazole	4 hr/149°	4235
	4 hr/149° + 1 hr/300°	6120

*4.0 parts per hundred resin (phr) unless otherwise stated

**Maximum measurable value; at this point none of the four test specimens had broken.

3.2 Preparation and Testing of Imidazole Lactate Salts

Reference to the latent properties of imidazole salts as epoxy curing agents has been made in the past; however, only general properties of the system have been reported (ref 10, 11). It was claimed that when the imidazole salt was mixed with an epoxy resin, the system would remain workable for two weeks, but would cure in minutes at 300°F. The systems of interest in these laboratories can tolerate temperatures of only 150-160°F, but further investigation of the properties of imidazole salts as epoxy curing agents was indicated.

The lactic acid salts of both imidazole and 2-methylimidazole were prepared. However, it was decided to study only the imidazole salt since it had a lower melting point and thus was more easily mixed with the resins than was the 2-methylimidazole salt.

Figure 4 compares the rate of cure at room temperature for the imidazole lactate and commercially available imidazole compounds.

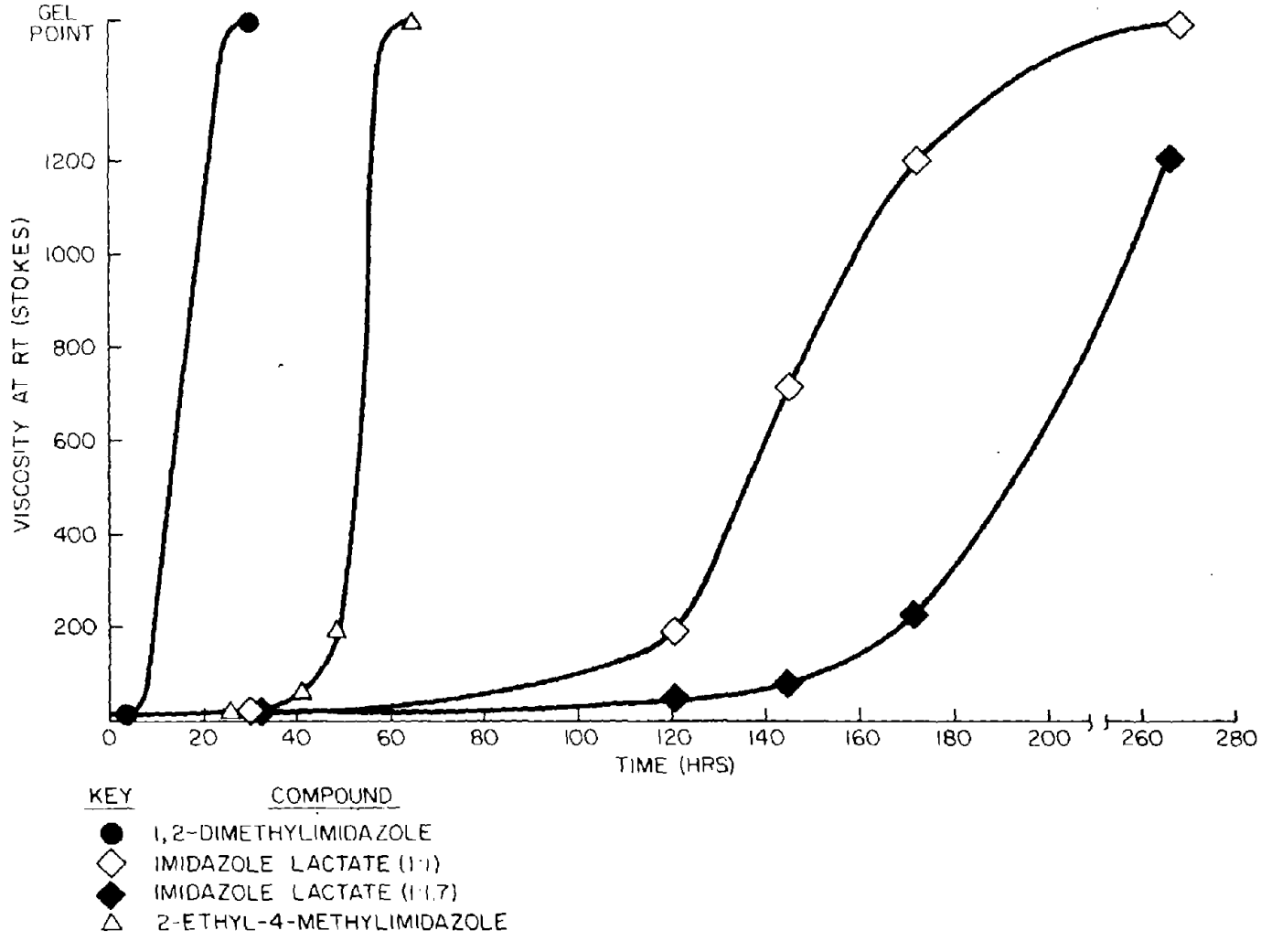


Figure 4. Change in viscosity at room temperature of a series of imidazole compounds

The imidazole lactate prepared from equal amounts of imidazole and lactic acid (1:1) gave a gel time at room temperature on the order of that obtained for the chloroalkylimidazoles. In the instance where excess lactic acid was employed (1:1.7), the gel time was much longer.

The investigation of the bond strengths and heat deflection temperatures obtained with the lactate (tables II and III) indicated a tremendous improvement over the values obtained with the deactivated imidazoles. However, comparison of these values with those obtained with commercially available imidazoles showed them to be inferior (ref 1). Also, the time required to effect a cure at 150°F was longer than desired. Therefore, the use of imidazole lactate as an epoxy curing agent did not result in the desired improvements, and no further experimentation with the system is planned.

Table III

Heat Deflection Temperature (HDT) of Epoxy Resin Cured with Imidazole Compounds

Compound	Cure Cycle (°F)	HDT (°F)
5-Chloro-1-ethyl-2-methylimidazole	185 hr/RT + 6 hr/149°	100°
	185 hr/RT + 6 hr/149° + 1 hr/300°	*
Imidazole Lactate (1:1)	185 hr/RT + 6 hr/149°	190°
	185 hr/RT + 6 hr/149° + 1 hr/300°	256°
Imidazole Lactate (1:1.7)	185 hr/RT + 6 hr/149°	181°
	185 hr/RT + 6 hr/149° + 1 hr/300°	243°
1-Methylimidazole	137 hr/RT + 4 hr/149°	189°
	137 hr/RT + 4 hr/149° + 1 hr/300°	291°
2-Ethyl-4-methylimidazole	137 hr/RT + 4 hr/149°	180°
	137 hr/RT + 4 hr/149° + 1 hr/300°	296°

* Specimen softened during the 300°-F postcure and was not suitable for testing.

3.3 Microencapsulation of Imidazole

An ideal method of rendering an infinite pot life to a mixture of epoxy resin and imidazole curing agent would be through microencapsulation. If the curing agent could be totally surrounded by an inert material, and released at the required time by means of heat or pressure or both, then the problem of extended pot life would be solved.

An attempt at encapsulation of imidazoles was made by another laboratory*. Liquid imidazole compounds were not amenable to their methods of encapsulation, so encapsulation of solid imidazoles was attempted using a copolymer of polyethylene and vinyl acetate. This particular capsular wall was soft and pliable and designed to release the imidazole under pressure, or at temperatures in the range 60-70°C.

When the capsules were tested, they were found to be as active for curing as unencapsulated imidazole. Also, when the capsules that contained 20 percent by weight of wall material were mixed with epoxy resin, they quickly floated to the surface of the resin.

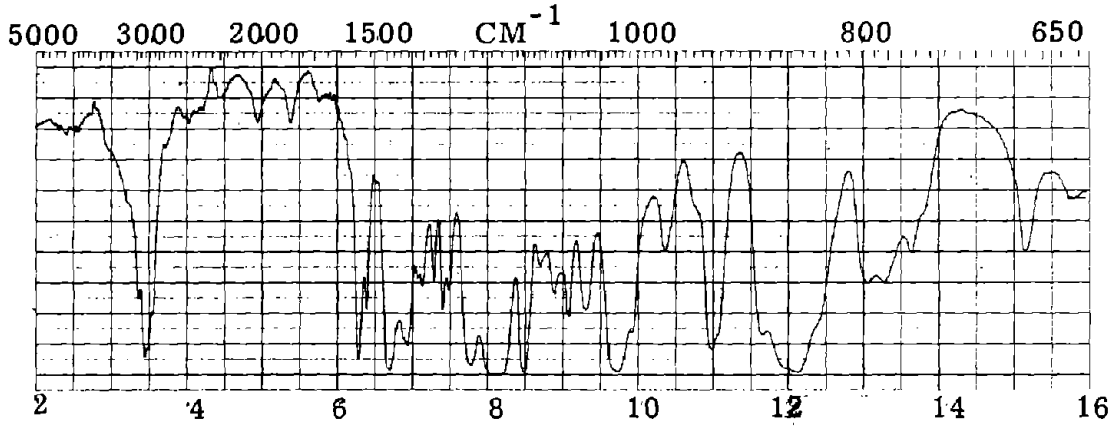
When the capsules were washed for only 5 min with cold water, 75-80 percent of the theoretical amount of imidazole was found in the aqueous extract. Apparently the polyethylene-vinylacetate walls were discontinuous, i.e., they contained openings which permitted passage of the imidazole and that accounted for the unexpected reactivity toward epoxy resins.

3.4 Imidazole Compounds as Catalysts for Epoxy-Polyurethane Systems

The cure of an epoxy resin with an imidazole compound results in some characteristic changes in its infrared spectrum. As shown in figure 1 for EMI-24, curing takes place in two steps. An initial attack on an epoxide ring by the nitrogen which is substituted with an active hydrogen results in the formulation of a secondary hydroxyl group. When 1-methylimidazole (MI-1) is the curing agent, this step cannot occur, and one should not observe a hydroxyl absorption in the infrared. Indeed this was the case with MI-1, in that no absorption at 3300-3500 cm^{-1} (-OH) was observed until the polymerization was nearly complete, while the epoxy absorption at 920 cm^{-1} disappeared quite rapidly. Figure 5 compares the infrared spectrum of an uncured and a cured mix of 1-methylimidazole and epoxy resin.

---

*Coordinated through Carl Schaab, Capsular Research Laboratory, National Cash Register Co.



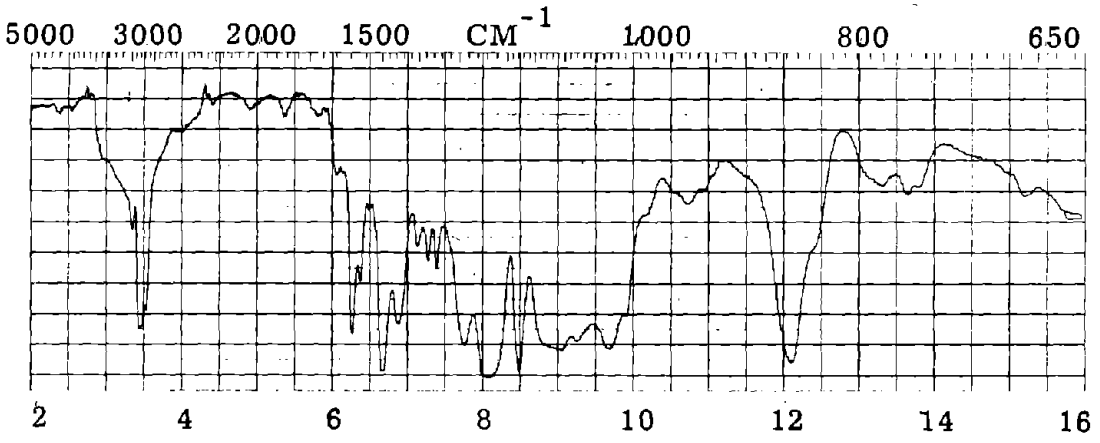
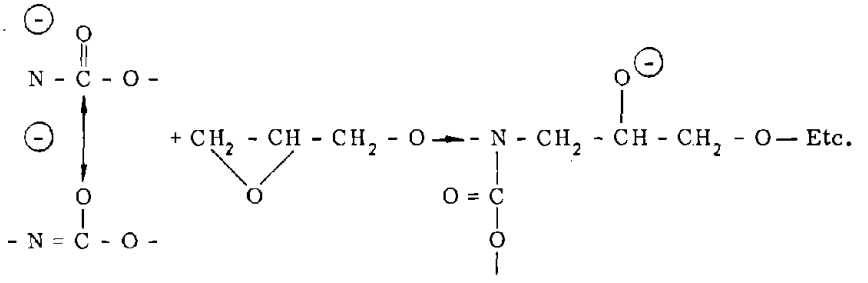


Figure 5. Infrared spectra of epoxy resin: 1-methylimidazole before and after curing

The polyesterurethane elastomer shows a characteristic infrared spectrum with absorptions at 3320 cm^{-1} (sharp, N-H) and 1730 cm^{-1} (strong, carbonyl).

In following the changes in the infrared spectrum during the cure of an epoxy-urethane system, a hydroxyl absorption (N-H) weakened. The urethane carbonyl (1730 cm^{-1}) broadened, an indication that some changes in the environment near the carbonyl might be occurring. With this evidence it appears that crosslinking reactions through the urethane bridge are occurring in this system, i.e., that the alkoxide ion of the imidazole-epoxy product

has abstracted the proton from the urethane linkage to yield an active species which then attacks the epoxy ring in the manner shown below.



Further evidence of crosslinking through the urethane bridge was obtained when the product of the epoxy-polyurethane-imidazole system was extracted with tetrahydrofuran (THF). Some polyurethane was abstracted into the THF (as shown by infrared absorption), but the bulk of the product remained insoluble.

3.5 Imidazole Compounds as Catalysts for an Epoxy-Polysulfide Rubber System

The discovery that some imidazole compounds effect a satisfactory cure in an epoxy-polysulfide rubber (PSR) system, while others are essentially unreactive, prompted an investigation to provide an explanation.

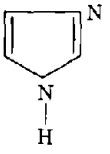
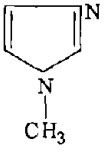
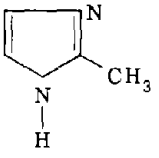
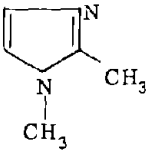
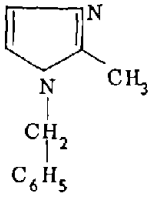
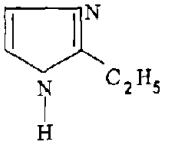
Initial studies were performed with a series of commercially available alkyl and dialkyl substituted imidazoles used as catalysts for 70:30 mixes of epoxy resin:PSR. Table IV lists the results of this study. It is evident that the only difference between the imidazoles that cure this system and those that do not is whether they are substituted in the 2-position of the ring. Those that are not substituted in the 2-position (i.e., contain a proton) are ineffective as catalysts for this system.

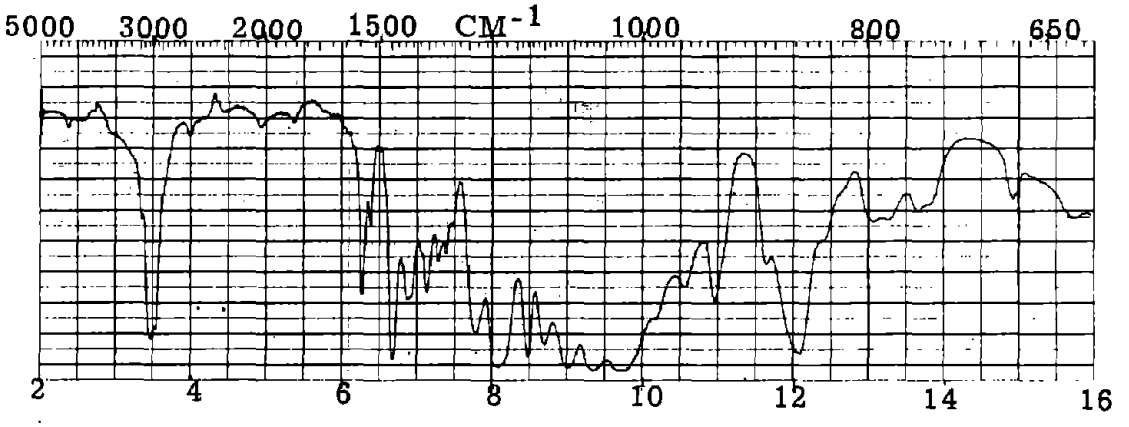
In an attempt to determine the difference in results, two imidazoles, one effective and one ineffective, were chosen for more detailed studies in which the curing reaction was followed via infrared absorption (IR). In order to simplify the system, both test imidazoles were substituted in the 1-position to prevent step 1 of the mechanism outlined in figure 1 from occurring. 1,2-dimethylimidazole represented the compounds that effected a cure, and 1-methylimidazole (MI-1) represented the one that did not cure.

In the following the cure of an epoxy-PSR mixture with 1,2-dimethylimidazole using IR, as shown in figure 6, the expected changes were observed. The loss of the mercaptan absorption (2525 cm^{-1}) and loss of the epoxy absorption (920 cm^{-1}), along with the formation of a hydroxyl absorption (3350 cm^{-1}), were easily detected. There was virtually no change in the region 1600-1800 cm^{-1}.

Table IV

Comparision of Alkylimidazoles as Catalysts for the Epoxy-Polysulfide Rubber (PSR) System

Compound	m.p.(°C)	b.p.(°C)	Results of a 300°F Cure with 70:30 Epoxy:PSR
	90°		After 24 hr at 300°F, the resin would flow when hot and stiffen at RT.
		190°	After 24 hr at 300°F, the resin would flow when hot and exhibit a consistency like gelatin at RT.
	135°		After 15 min at 300°F, the resin cured with a violent exotherm.
	35°		After 15 min at 300°F, the resin cured with a violent exotherm.
		125-7° (3mm)	After 15 min at 300°F, the resin cured with a violent exotherm.
	40-42°		After 15 min at 300°F, the resin cured with a violent exotherm.



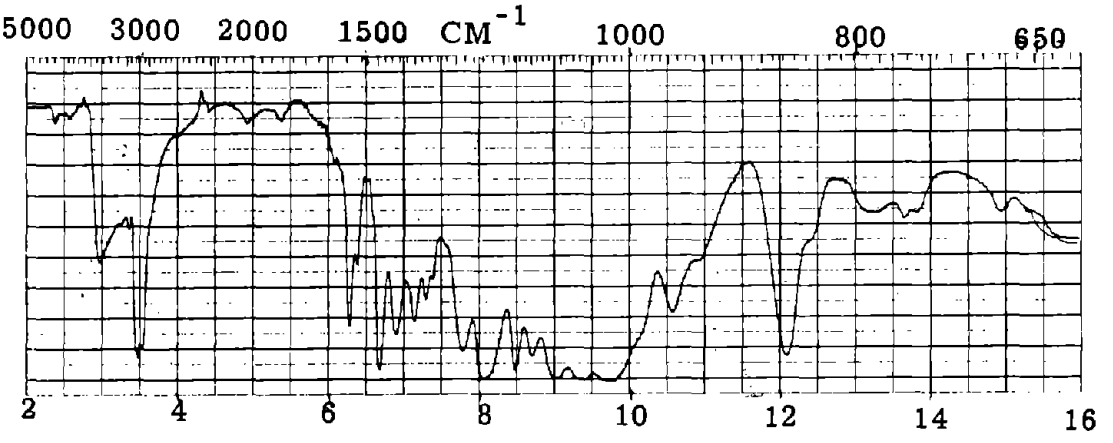
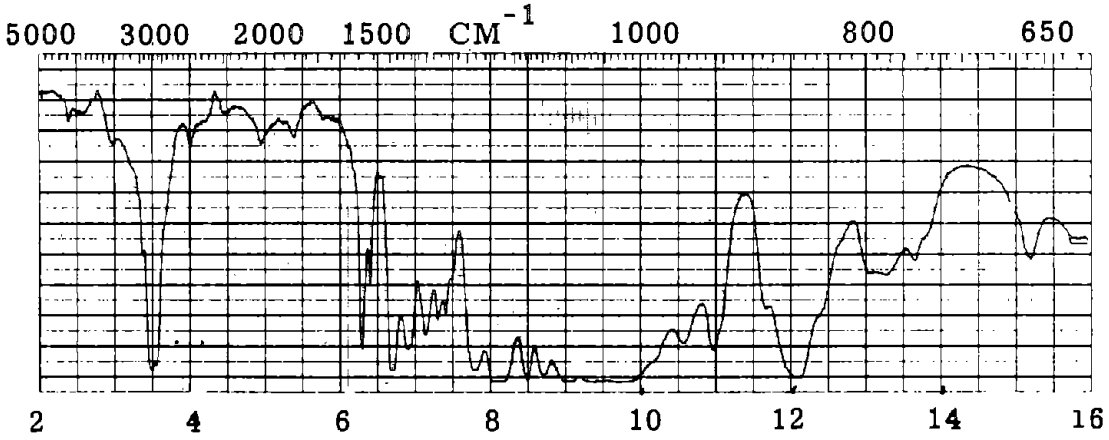


Figure 6. Infrared spectra of epoxy resin: polysulfide rubber: 1,2-dimethylimidazole before and after curing

Figure 7 shows the IR spectra of an epoxy-PSR mixture, before and after an attempted cure with MI-1. As observed in the curable system mentioned above, a loss of mercaptan absorption (2525 cm^{-1}) and of epoxy absorption (920 cm^{-1}) and the formation of a strong hydroxyl absorption (3350 cm^{-1}) occurred. However, a new and very strong absorption was observed at approximately 1665 cm^{-1}. In systems that would not cure properly, this unexplained absorption was always found in the IR spectrum of the heated mixture.



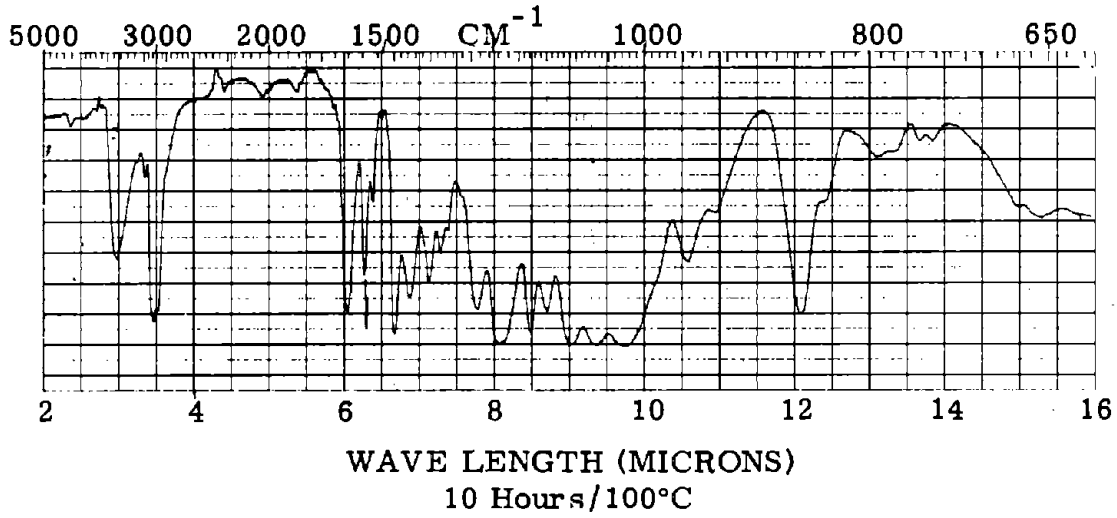
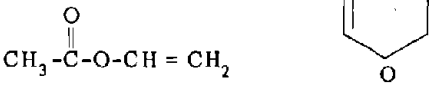


Figure 7. Infrared spectra of epoxy resin: polysulfide rubber: 1-methylimidazole before and after curing

By means of IR it was determined that the heating of any two of the three components together did not result in the formation of an absorption at 1665 cm^{-1}. It also was determined that the imidazoles and PSR do not undergo any reaction, and a mix of epoxy and PSR would react only slowly at elevated temperatures. From this information it is evident that no matter what is causing the absorption at 1665 cm^{-1}, the first step in the reaction has to be the opening of an epoxide ring via an imidazole attack.

A series of studies in which the ratios of epoxy, PSR and MI-1 were varied was performed. Results showed the appearance of an absorption at 1665 cm^{-1} even when very small amounts of MI-1 and PSR were present. On the other hand, if an excess* of PSR over epoxy was employed, then the band at 1665 cm^{-1} was not evident in the IR. Therefore, it seems that the MI-1 and PSR were essentially behaving as catalysts. Replacement of the PSR with a small amount of water caused an absorption at 1665 cm^{-1}, but, when ethanol was used, this peak did not appear.

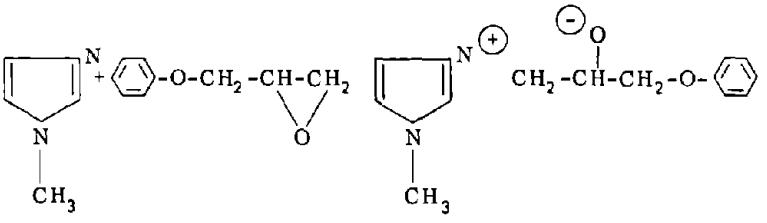
Unsaturated ethers and esters are known to absorb in the region 1600-1670 cm^{-1}. In a check of the IR spectra of vinyl acetate and dihydropyran, a strong absorption near 1660 cm^{-1} was observed.



Vinyl acetate

Dihydropyran

Further proof of the necessity of having unreacted epoxy resin present and of the initial step in the mechanism that ultimately results in the formation of the 1665 cm^{-1} absorption was obtained from a series of reactions involving the reaction product between phenylglycidyl ether and 1-methylimidazole.



*Based on molecular weight per reactive function. Therefore, 2.5 mole-equivalents of PSR equals 1.0 mole-equivalent of epoxy resin.

When this addition product was treated with PSR, essentially no reaction was observed. However, when it was treated with a mixture of epoxy and PSR, an exothermic reaction took place, and the IR showed an absorption at 1665 cm^{-1}.

Isopropyl glycidyl ether was treated with PSR and MI-1 in the hope that the product of the side reaction could be isolated. After the mix had been heated for 4 hr at 100°C, it was distilled under reduced pressure. About 30 percent of the initial isopropyl glycidyl ether was recovered along with a higher boiling material. The higher boiling distillate gave an IR spectrum containing a strong hydroxyl peak (3350 cm^{-1}), unknown peak (1665 cm^{-1}) and no epoxide peak (920 cm^{-1}). Thin-layer chromotography using silica gel with 1:1 benzene:ether indicated that the material was mainly one component with small amounts of 3 or 4 other materials.

The nuclear magnetic resonance (NMR) spectrum of the high boiling distillate (fig. 8) was compared to the NMR spectra of the starting materials (fig. 9). The comparison shows that the distillate contains an isopropyl group (1.0-1.3σ) but is free from unreacted epoxide (2.3-2.7) and (3.6-3.8σ). The aromatic imidazole protons are absent (6.9 and 7.4σ), but a new distinctive pair of doublets (6.1-6.4σ) is present.

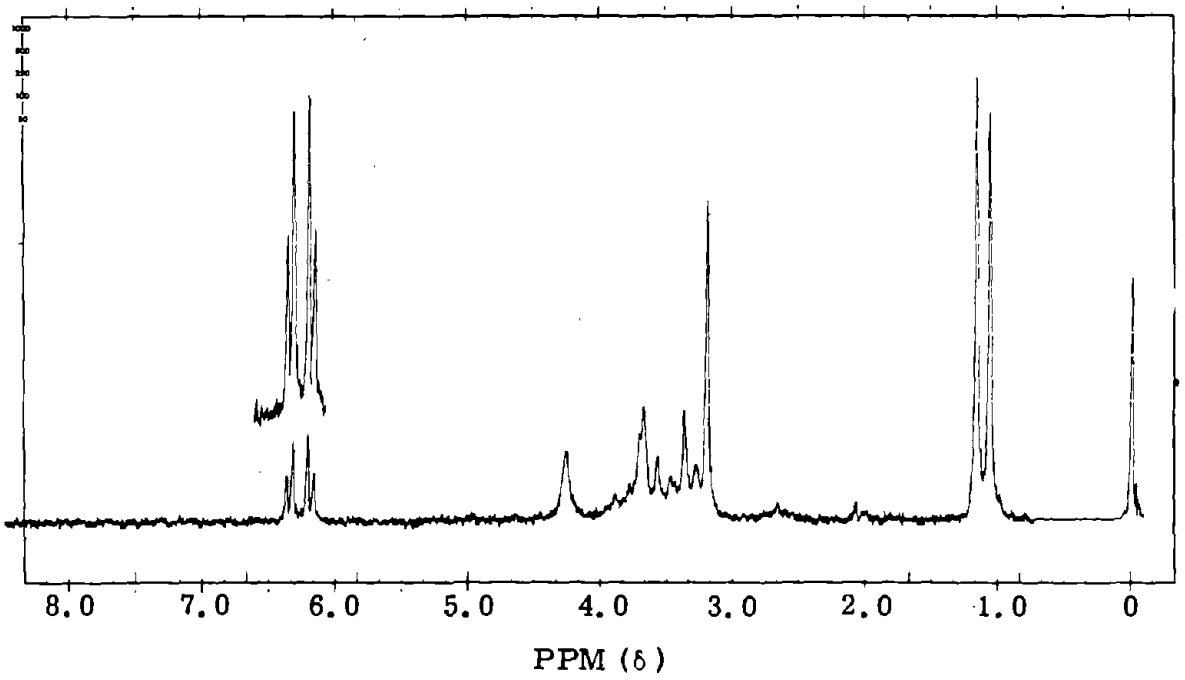


Figure 8. NMR spectra of distillate, bp 140°C/0.2mm Hg (peaks between 6.1 and 6.4 δ also shown expanded for clarification)

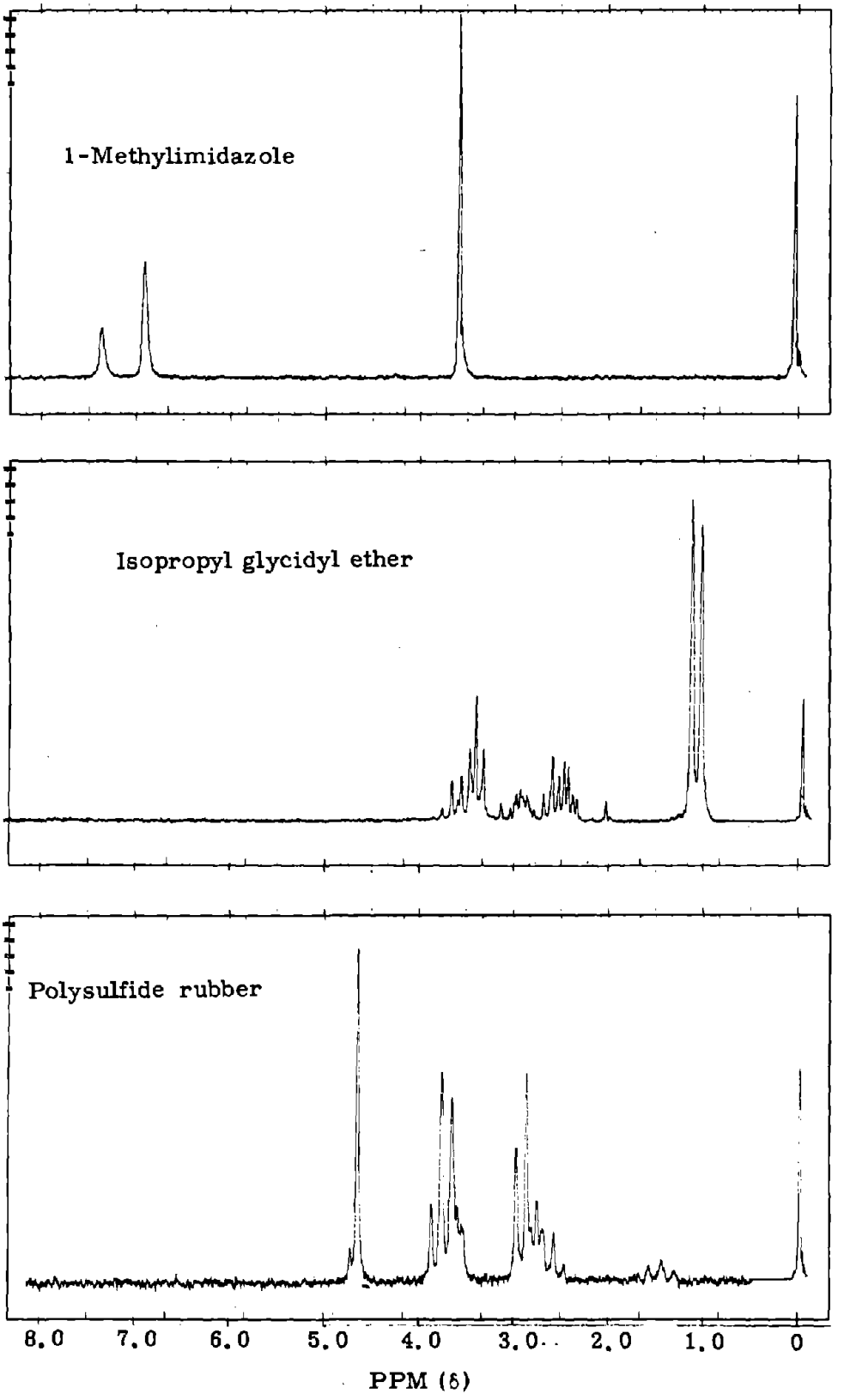
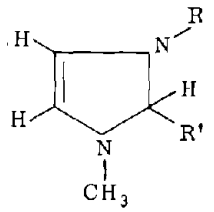


Figure 9. NMR spectra of starting materials

Microanalysis showed that the distillate contained 53.1 percent carbon, 8.6 percent hydrogen, 10.3 percent nitrogen and a trace amount of sulphur.

The presence of nitrogen in the distillate indicates that 1-methylimidazole, or a derivative, appears in the product. The absence of peaks attributable to the aromatic imidazole protons, and the appearance of a pair of doublets at 6.1-6.4σ, indicate that the MI-1 has been converted to a dihydroimidazole. This loss in aromaticity is also indicated by a shift in the peak attributed to the N-methyl group from 3.6 to 3.2σ.



Dihydroimidazole

Attempts to write a mechanism that accounts for the observations has not been successful. This side reaction involving some imidazole compounds is unexpected. Since the tertiary nitrogen of the imidazole ring is the reactive site for polymerization (as previously reported in ref 1), substituents at the 2-position of the ring should not have any effect on the curing.

The observed differences in curing effects of imidazole compounds on the epoxy-PSR system show that the imidazole system is not as simple and straightforward as first reported by Farkas and Strohm (ref 12).

The collected facts on this system are:

(1) PSR and MI-1 are necessary in the reaction causing the absorption at 1665 cm^{-1} observed in the IR.

(2) This absorption does not occur when an excess of PSR over the epoxy resin is used.

(3) The first step in the reaction has to be an imidazole attack on an epoxy ring.

(4) The only difference in the imidazoles that do or do not cure is whether they are or are not substituted in the 2-position.

(5) Water can take the place of PSR in causing the formation of the absorption at 1665 cm^{-1}.

(6) The failure of MI-1 in the epoxy-PSR system is due to the deactivation of the catalyst by its conversion to the dihydroimidazole derivative.

3.6 Future Work

(1) Further attempts to increase the pot life of epoxy-imidazole adhesive systems will be discontinued in favor of an investigation into low-energy rapid-curing systems for encapsulation.

(2). Synthesis of alkyl imidazole substituted in the 2-position with a phenyl or a tert-butyl group would yield valuable information as to whether the reactivity of the 2-alkylimidazoles tested thus far derives from their benzylic-type protons.

(3) Further investigation in the area of microencapsulation in plastic capsules will depend on work being performed at the National Cash Register Capsular Research Laboratory.

4. CONCLUSIONS

Bond strength, heat deflection temperature, and gel time studies indicate that none of the chloro, chloronitro, or cyanonitro substituted imidazoles were satisfactory epoxy curing agents under the desired conditions.

Measurement of the same parameters using imidazole lactate as the curing agent gave results that were more encouraging. While imidazole lactate was found unsuitable for applications requiring moderate cure temperatures (i.e., 140-160°F), it was found to exhibit excellent properties when cured at high temperatures (i.e., 250-300°F).

Current techniques in microencapsulation preclude its use with liquid imidazoles. The attempt at encapsulating solid imidazole yielded poor results.

The use of imidazole compounds in an epoxy-polyurethane system causes crosslinking and the formation of a copolymer.

Imidazole substituted in the 2-position with alkyl groups will effect a cure of a polysulfide rubber flexibilized epoxy resin. Imidazoles unsubstituted in the 2-position (i.e., the position contains a proton) will not effect a cure of the polysulfide rubber-epoxy system.

5. REFERENCES

1. T. J. Dearlove, HDL-TR-1551, "Epoxy Curing Agents, I. Imidazoles."

2. T. J. Kilduff, unpublished results from this laboratory.

3. Estane Polyurethane Materials, B. F. Goodrich Co., 64-14, p. 6, 10; 64-18, p. 15.

4. J. A. Clarke and J. M. Hawkins, Preprints of the 155th ACS Meetings, Div. of Organic Coatings and Plastics Chemistry, April 1968, p. 468.

5. Handbook of Epoxy Resins, H. Lee and K. Neville. McGraw-Hill Book Co., New York, N. Y. (1961) 1. 16-21 to 16-29.

6. G. E. Trout, and P. R. Levy, Recucil. 84, 1257 (1965).

7. G. E. Trout, and P. R. Levy, Recucil. 85, 765 (1966).

8. O. Wallach, Ann. 184, 33 (1877).

9. O. Wallach, Ann. 214, 257 (1882).

10. D. Warren, U. S. Patent 3,356,645.

11. C. C. Anderson, Ind. Eng. Chem., 60(8), 80 (1968).

12. A. Farkas and P. F. Strohm, J. Appl. Polymer Sci. 12, 159 (1968).